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by

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REDUCTION OF THE BIOCHEMICAL OXYGEN DEMAND OF SEWAGE BY CHLORINATION

By H. G. Baity[1] and F. M. Bell[2]

As an introduction to this discussion of the effects of chlorine in reducing the biochemical oxygen demand value of sewage, let us consider a few of the very elementary facts regarding the nature of sewage and the reasons for its treatment—facts which are assumed to be generally known, but which are basic in dealing with problems of waste disposal and stream sanitation.

The Nature of Sewage

Physical Characteristics: Sewage is the spent water supply of a community, which carries the various domestic and industrial wastes that have been contributed to it in passing through plumbing fixtures and industrial processes. We are accustomed to regard it as a substance extremely foul and dangerous, entirely unlike the pure domestic water supply from which it is derived. This conception is well justified, but in physical character sewage is not so different, after all, from its former state. It still contains more than 99.9 per cent of water. It may be turbid and colored, but less than 0.1 per cent of its weight consists of solid materials, suspended and dissolved, which the water has taken up in being used. Part of these solids, about one-sixth, are rather large and coarse in nature, and may be readily settled out; part of them, about one-quarter, are in a colloidal state, and remain suspended in the liquid indefinitely; while yet another part, more than one-half, are dissolved in the water.

Pollutional Characteristics: Each of these three physical forms of sewage solids—settling, colloidal and dissolved—is composed in part of mineral, or inorganic, materials which are stable and do not tend further to decompose. About 50 per cent of the total solids content of average sewage is of this character which does not offend or trouble us. If all of it were mineral in nature the problems of stream pollution and sewage treatment would not exist. But, alas, the other 50 per cent of the solids gives us grave concern, the organic

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materials in the three physical states which are unstable in character, and which are decomposed through natural bacterial activity to produce conditions which may be offensive to the senses. The major function and perplexing problem of sewage disposal is the satisfactory handling of this organic class of solids which constitutes only 0.05 per cent of the sewage weight, a trifling one pound per ton of raw sewage! This organic class of solids—settling, colloidal and dissolved—constitutes what is termed *pollution.* Pollutional materials in the presence of moisture are attacked by bacteria and are decomposed by the biochemical process of oxidation. The bacteria require oxygen for their work. If an oxygen supply is available in solution in the medium adequate to supply the demands of the bacteria, an aerobic condition is said to exist, and the bacterial destructon of the organic matter proceeds as an oxidizing process, without the production of offensive conditions. If an inadequate supply of dissolved oxygen is available for the life processes of the bacteria, they, still requiring oxygen, break down the molecules of the dissolved solids to obtain it. For example, the sulphate radical SO_4 is robbed of its oxygen and *reduced* to a sulphide substance. As a consequence, anaerobic conditions prevail, obnoxious odors are produced, bubbling of the evolved gases takes place, and an unsightly black discoloration occurs. Thus, if sewage is discharged at a given rate into a flowing stream, and if the water of the stream contains a sufficient quantity of dissolved oxygen to meet the demands of the bacteria decomposing the organic matter present, biochemical oxidation proceeds unnoticed, and no offensive septic action takes place. If the oxygen supply of the stream water is insufficient to meet the demands of the decomposing bacteria, an extremely noisome condition of the stream prevails. Since the amount of oxygen which water is capable of taking into solution is very limited, it is apparent that the quantity of water in a stream is the variable factor of greatest importance and that a fairly accurate limit can be derived for the amount of sewage of a given strength that a given stream flow is capable of taking care of. This leads naturally to the definition of the measure which is applied to wastes for determining their pollutional qualities. This measure is known as Biochemical Oxygen Demand. It is determined by laboratory experiment, conducted so as to simulate the conditions of nature. By incubation of a sample of sewage or waste in a suitable dilution of oxygenated water, which

is seeded with bacteria and kept at average natural temperature (20°C) for a given period of time (usually 5 days), the oxygen depletion can be obtained. From the measured depletion the biochemical oxygen demand under these standard conditions is computed and expressed as parts per million, by weight, on the basis of the original sample. Thus, a sewage with a 5-day B. O. D. of 100 p. p. m. indicates that in five days each million pounds of sewage will require 100 pounds of oxygen to satisfy the demand of the biological life which is engaged in decomposing its organic materials.

Bacteriological Characteristics: In the transformation of water into sewage the greatest change in character is found in the bacterial content. Water supplied to consumers from modern purification works is practically sterile, and never contains a disease-producing organism. Average fresh sewage contains from 2,000,000 to 4,000,000 bacteria in each cubic centimeter (15 drops). This phenomenal increase in bacterial population in the spent water is due largely to the enormous numbers of organisms contained in the excreta of human beings. Investigators have found that a normal adult man discharges in his feces an average of 33,000,000,000,000 (33 million million) bacteria per day, in addition to other millions contributed by his skin and urine. These organisms, known as colon bacilli, are normal to the human, and are always found in such numbers in their discharges. Colon bacilli, being the natural inhabitants of all people, are, in themselves, harmless. So, most of the organisms contained in sewage are not of the pathogenic, or disease-producing, kind. On the contrary, they are of genuine importance and value in the economy of nature through the scavenger work which they accomplish. *But,* if a person discharging sewage happens to be infected with the organisms of any of the intestinal diseases, such as typhoid fever, then these organisms will be discharged in quite as great abundance as the normal colon bacilli, and will readily infect people who accidentally or ignorantly take these organisms into their mouth and digestive system.

The Objectives in Sewage Treatment

In the treatment of sewage there are two problems to be considered, either or both of which may be important, depending upon the nature and the use of the stream into which the sewage is discharged. These functions of treatment, stated in order of their

significance, are, (1) to decrease the bacterial content of the sewage for the protection of the public health, and (2) to decrease the pollutional content so as avoid nuisance conditions in the receiving stream. Where a stream is to be used for water supply or recreational purposes the removal of bacteria is the primary objective; where it has no such use, but has a flow of water which is incapable of carrying away the wastes and furnishing oxygen for their bacterial stabilization, the reduction of pollution load is of major importance. The former is a hygienic problem of getting rid of living, disease-producing organisms, and affects public health directly; the latter is mostly an aesthetic problem of taking out of the sewage the foul, putrescible matter that would become offensive to the senses, and affects the public health only indirectly. In sewage treatment practice it is necessary to consider for each individual case which of these functions is of paramount importance, and the degree of removal of organic materials or bacteria, or both, that is demanded.

Methods of Accomplishing Objectives

These two objectives in sewage treatment may be attained in a variety of ways. Usually it is desirable to remove both bacteria and organic constituents to certain degrees, and, fortunately, most of the facilities for sewage treatment, natural and artificial, accomplish to some extent the two objectives at the same time. If conditions permit, sewage may be discharged untreated into a stream, in which case the natural agencies of sedimentation and oxidation are utilized to take care of the pollutional and bacterial load. This is known as "disposal by dilution" and the natural processes constitute "self purification." Where the avoidance of nuisance is the only problem involved this method of disposal may be used, provided the stream flow is sufficiently large. And how great must the discharge be for a given quantity and quality of sewage? A dependable estimate may be made by simple calculation. The water of a clean stream at normal temperature can hold in solution about 9 parts per million of oxygen. Assuming a raw sewage with a 5-day biochemical oxygen demand of 180 p. p. m., and neglecting augmentation of flow and reaeration of the stream, the ratio of dilution water to sewage would have to be 180/9, or 20, to satisfy the 5-day oxygen requirements.

If the minimum dry-weather flow is only two-thirds of that amount, then the sewage must be treated so as to reduce its B. O. D. by one-third, to a value of 120 p. p. m. This could be accomplished by sedimentation. Or, if the minimum stream flow were one-tenth of that required for the disposal of raw sewage without nuisance, the sewage would require treatment which would reduce its B. O. D. to one-tenth of its raw value, or 18 p. p. m. Sedimentation with a secondary oxidizing treatment, such as is provided by trickling filters, would provide this efficiency. Various combinations of treatment devices may be employed to produce any desired efficiency in biochemical oxygen demand reduction. If bacterial reduction is the problem, this may likewise be accomplished to any desired degree by judicious employment of combinations of sedimentation, oxidation and disinfection units.

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Sedimentation devices which are commonly used in sewage treatment are septic tanks, Imhoff tanks and mechanical clarifiers, the function of which is to remove the settling solids. They may reduce the B. O. D. of sewage by 30 to 35 per cent, but their bacterial efficiency is low. Secondary oxidizing devices, such as trickling filters, contact beds, sand filters and activated sludge, are employed for further removal of suspended and dissolved organic solids and bacteria. They may be depended upon for a B. O. D. reduction of 80 to 95 per cent, and a bacteria reduction of 90 to 99 per cent. Disinfection devices using chlorine gas, or chloride of lime, are used extensively for bacterial reduction in raw, settled and filtered sewage, and with proper operation show an efficiency of about 99 per cent.

Purpose in Chlorination Study

For more than 20 years chlorine has been used as a sterilizing agent for bacterial destruction in water purification and sewage treatment works. Its germicidal properties have been well investigated experimentally and proved by practice, so that it has now become almost universally used where high degrees of bacteria removal are desired. But not until the last year or two has chlorine been considered as an agent capable of reaction with the organic materials of sewage in such a way as to reduce the biochemical oxygen demand. Several investigators have found an indication of such an effect in laboratory-scale experiments, and it is understood

that others have recently observed the same phenomenon in plant-scale experiments under operating conditions. With ideal conditions for such a study existing at the Chapel Hill sewage treatment plant, an investigation was begun in the spring of 1928, and continued for two months on a plant-size scale, to determine the effects on the biochemical oxygen demand of settled sewage of various dosages of chlorine. This study is one part of an extensive program of investigation on the uses of chlorine in sewage treatment which is in progress.

METHODS AND TECHNIQUE

Chapel Hill is a university town of about 5,500 inhabitants, and has no industries. The sewage is therefore strictly domestic in character and relatively weak, but carries a considerable amount of grease from the dining halls and restaurants. The average daily flow is about 450,000 gallons, and reaches the treatment works about 1¼ miles from town in a fresh state. The treatment plant consists of bar screens, a circular Imhoff tank and sludge beds. The tank is heavily overloaded, the retention time of the sewage in the flowing-through chamber being only 45 minutes, and the removal of settling solids is only 75 to 85 per cent. The settled sewage is discharged directly into a small stream with highly variable flow.

Chlorination Apparatus: For the purposes of this and other experiments, a solution-type Wallace and Tierman chlorinator, with a capacity of 50 pounds per day, was installed at the plant, and so arranged that the chlorine solution could be applied either to the influent or effluent of the Imhoff tank. For this study the chlorine was introduced into the effluent sewage in a manhole immediately below the plant, where ideal mixing was obtained. Samples of the chlorinated sewage were taken from another manhole about 300 feet farther down the line between the tank and the creek. Samples of the unchlorinated sewage were collected from the effluent channel of the tank. The rates of chlorine application during the experiment were varied from 5 to 15 parts per million, on the basis of the sewage flow.

Time of Experiment: The period covered by this study was April 17 to June 2, 1928. During this time the conditions governing the quantity and quality of the sewage were practically stable. The

temperature of the effluent sewage varied between 13° and 20° C, and the pH between 6.6 and 6.9.

Sampling: By simultaneous sampling of the chlorinated and unchlorinated sewage, the samples were identical in all respects except for the applied chlorine. To further insure this condition, the daily samples were taken over a period of one to two hours at 10 minute intervals, at the same time each morning when the flow was fairly constant, and composited. The free chlorine content of each subsample of chlorinated sewage was determined after 10 minutes' contact and the results averaged. The temperature, pH, rate of chlorinator feed and rate of sewage flow were taken several times during the sampling period and the results averaged to obtain the mean.

Laboratory Technique: Immediately after sampling the samples were taken to the laboratory, and dilutions made for biochemical oxygen demand. The dilution method was used for this test. The water used for dilution was distilled water, fully oxygenated and containing 500 p. p. m. of sodium bicarbonate, which had been stored in the laboratory for several weeks at constant temperature. The incubation bottles were chemically clean, and were sealed in a water bath during incubation. The proper dilution factor was determined by experiment. Dilutions were prepared in clean glass jars, those of the chlorinated sewage being tested each time for residual chlorine. In most cases the free chlorine disappeared after dilution, otherwise the jars were allowed to stand until there was disappearance. The chlorinated dilutions were then reseeded with 1 c. c. per liter of unchlorinated sewage that had been strained through cotton, and in the computations correction was made for this seeding material. Duplicate sub-samples were run for chlorinated and unchlorinated samples, and a dilution-water blank was also incubated. The temperature of incubation was 20°C., and the time was 5 days. Once a week additional samples were run for the 1 and 15-day demands. The Winkler method was used for all dissolved oxygen determinations. Results for each series were averaged, corrections applied, and the B. O. D. values calculated.

Results: It was found that a chlorine dosage of less than about 7.5 p. p. m. produced no residual after 10 minutes contact; about 9 p. p. m. was required to give a residual of 0 to 0.1 p. p. m.; from 10 to 12 p. p. m. for a free chlorine excess of 0.2 p. p. m.; and

12 to 15 p. p. m. to produce a residual of 0.5 p. p. m. The temperature of the sewage within the limits of the experiment did not appear to affect these relationships, nor did it seem to have any effect on the reduction of biochemical oxygen demand. The pH values of chlorinated and unchlorinated samples were in all cases the same. The biochemical oxygen demand of the unchlorinated settled sewage ranged between 36 and 148 p. p. m. during the period of the experiment, with a mean of 86. The results showing the effect of chlorination on reduction of biochemical oxygen demand are summarized in the following table, indicating the B. O. D. decrease accompanying different amounts of residual chlorine. These computations have been made by averaging the results in each residual-chlorine group.

Chlorine Dosage p. p. m.	Residual Chlorine 10 min., p. p. m.	B. O. D. Unchlorinated Samples, p. p. m.	B. O. D. Chlorinated Samples, p. p. m.	Per Cent Reduction
5-7.5	0	77.0	71.1	7.4
8- 9	Trace	94.3	79.6	15.5
10-15	0.2-0.5	85.2	58.6	42.7
All samples (39)		85.8	48.9	31.7

When chlorine was applied in quantities insufficient to give a residual after 10 minutes contact there seemed to be little effect on the B. O. D. In samples dosed with 5 or 6 p. p. m., or about one-half the dose required to give a 0.2 p. p. m. residual, there was practically no decrease. With a dosage of about 9 p. p. m., about three-quarters that required for a residual of 0.2 p. p. m., there was observed an appreciable oxidation effect. The maximum effect of 42.7 per cent reduction in B. O. D. was found with a dosage of 10 to 15 p. p. m. and an excess-chlorine value of 0.2 p. p. m., or greater. However, it was observed that in samples heavily chlorinated and with residual chlorine in excess of 0.2 p. p. m. the results obtained were little, if any, better than those found with a 0.2 p. p. m. excess.

It seems uneconomical and wasteful to apply chlorine in greater concentration than that necessary to give this value. Owing to the wide hourly fluctuations in sewage flow, the matter of adjustment of dosage presents a problem. If the feed of the chlorinator is set for the peak flow, there is wastage of chlorine; if it is adjusted to the mean flow, the peak flows go under-treated and with the B. O. D. practically unchanged. It is the peak flows that demand treatment

most. With plants other than very small ones, it would be advisable to install automatic chlorinating equipment, or else proportion the chlorine dosage to the sewage flow manually.

The one-day biochemical oxygen demands on samples which had been fully chlorinated were found to be very low in comparison with the 5-day demands—much lower than the theoretical formula would give, although the samples were seeded. This indicates a delay in bacterial activity, due to the chlorination. In samples incubated for 15 days there was observed about the same relative decrease in B. O. D. in the chlorinated portions as was found for 5 days, indicating that there is a real oxidizing effect, a true biochemical oxygen demand reduction.

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Practical Application of Results

The applications of these results to actual practice are almost too obvious to require elaboration. From the previous discussion of the principles involved in sewage disposal, it is easy to see that a process capable of decreasing the oxygen requirements of liquid wastes by 30 to 40 per cent may have many uses that are important and economic. Actually, it is the same thing as providing means of increasing stream-flow by the same amount. It is certainly not a cure-all, nor a process which will supplant other established types of treatment. But when used judiciously, it seems entirely possible that chlorination may be of even greater service to the sewage treatment world than it has been in the past.

If there were no effect on the organic constituents of sewage, chlorine treatment would doubtless be justified in many cases for the retarding action it exercises on bacterial decomposition. By its use the intense biological activity requiring a large oxygen supply could be delayed until the pollutional material has been carried downstream to a point where, by increased dilution, the oxygen requirements can be met. But with actual reduction in the biochemical oxygen demand, and with high efficiency as a bactericidal agent, chlorine has three strong arguments to recommend it. Some examples of the use of chlorine as an oxidizing agent are the following:

(1) For treatment of raw sewage where the receiving stream has scarcely enough flow for its assimilation.

(2) For retarding decomposition in a small stream until the sewage can be carried to a point downstream where adequate dilution is afforded.

(3) As a permanent adjunct to treatment plants which, although functioning efficiently, are not affording the required degree of treatment.

(4) As an adjunct to treatment works that are overloaded and functioning inefficiently.

(5) For intermittent use on raw, settled or filtered sewage during the dry seasons of the year when stream-flow is at a minimum.

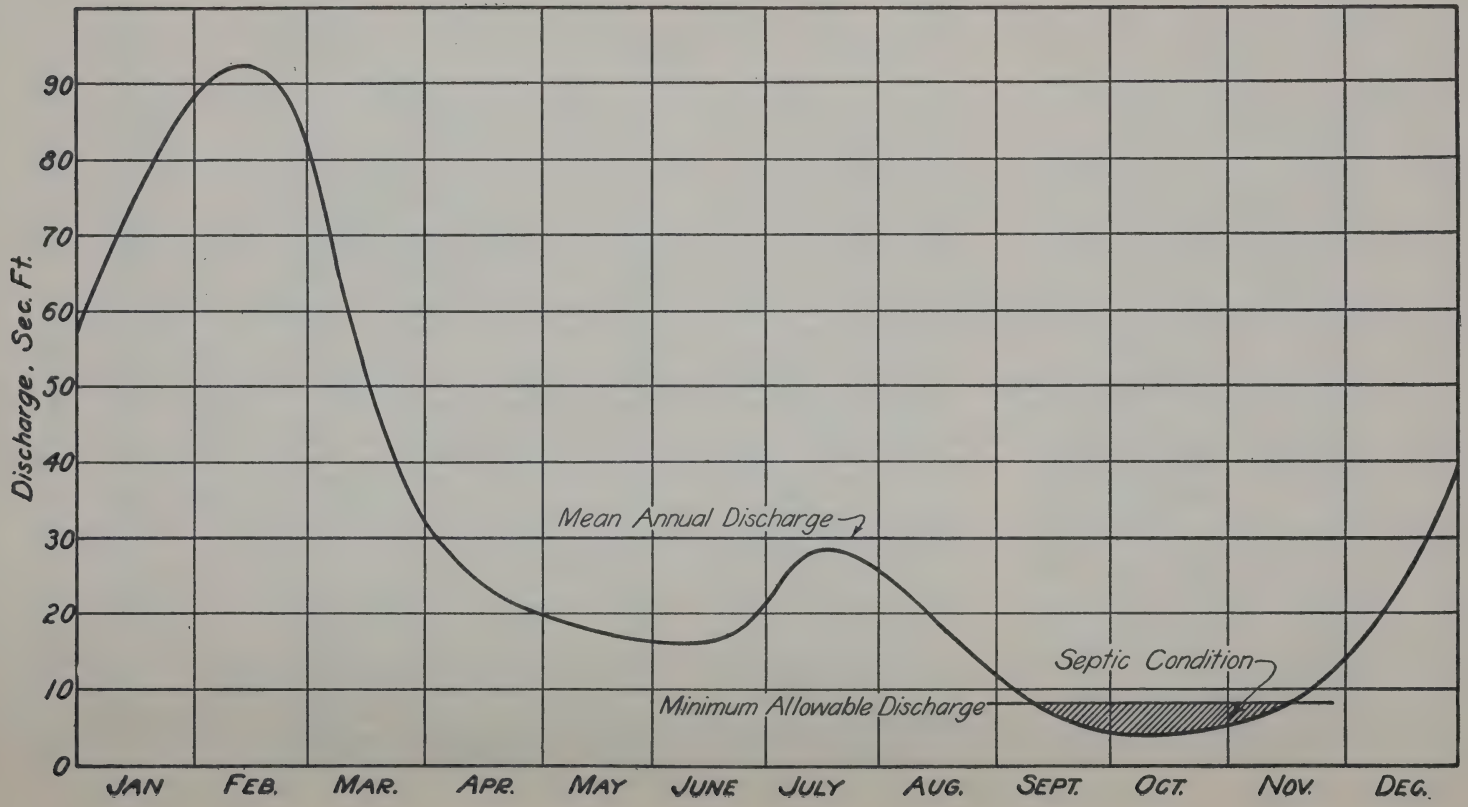
This latter use of chlorination appears to be the one of greatest utilitarian and economic significance. Sewage treatment plants must be designed for conditions of *minimum* stream flow, and, unfortunately, in all parts of the country there is a wide seasonal variation in discharge. It is believed that much money could be saved by building treatment works with capacities and efficiencies based on 150 per cent of the minimum stream flow, and depending upon chlorination to handle 35 per cent of the load during the critical periods. This can be illustrated more clearly by means of an example.

In the accompanying figure is shown a smoothed hydrograph for a typical small stream in North Carolina, which illustrates the wide monthly and seasonal variations in flow that are characteristic of such streams in this section of the country.

The minimum mean monthly flows frequently amount to only 10 to 12 per cent of the mean annual flows, while the minimum mean daily flows are often below 5 per cent of the mean annual discharge. Moreover, these depressions in flow occur during the late summer and early fall months, when temperatures are high and rates of biochemical oxygen demand greatest.

Let it be assumed that the stream shown in the figure receives one million gallons per day of settled sewage having a 2-day B. O. D. of 50 p. p. m. To avoid nuisance conditions, the required stream-flow would have to be about 8 cu. ft. per sec. The hydrograph shows that such a discharge is maintained during most of the year, but from early September until late November the flow is below the allowable minimum. To provide for this critical condition two alternatives exist: some form of secondary treatment, such as trick-

SMOOTHED HYDROGRAPH FOR SUGAR CREEK, CHARLOTTE, N. C., FOR 1926, SHOWING ESTIMATED EFFECT OF 1 M. G. D. SETTLED SEWAGE



ling filters, must be added to the plant; or chlorination may be employed temporarily to tide over the three months' period.

Cost of Chlorination

The advantage in the use of chlorine under such conditions is apparent when costs are considered. In the case given above the cost of addition of trickling filters to the 1 M. G. D. treatment plant would be about $60,000. The fixed charges, covering interest, sinking fund and depreciation would amount to about $8,000 per year. Units of this type must of necessity be in service all of the time to maintain their efficiency, and the annual operating cost would be about $1,800. This amounts to a total cost per year of $9,800. If chlorination were employed, the apparatus could be installed for $1,500, or less, and would be operated only when stream-flow conditions demanded it. The fixed charges for such an installation would be about $300 a year, and the cost of operation for 3 months each year, including repairs and chlorine, is estimated at $700, a total yearly expense of $1,000, or about one-tenth the cost of trickling filters.

This example is given only to illustrate the possibility of economic use of chlorine in such special cases. It should be clear that other types of treatment are not supplanted. Chlorination is limited in efficiency, and cannot be employed alone where a high degree of removal of organic solids is required. But it may be used to supplement other processes. Each type of treatment has its proper place and use; chlorination is merely a newly-recognized form of oxidizing treatment that will find its place.

Conclusions

From this study the following conclusions may be drawn:

(1) That chlorine treatment of sewage does exercise a very marked effect in reducing the biochemical oxygen demand.

(2) That its application in amounts insufficient to produce a residual causes a positive, but small, degree of oxidation. It was found that dosages of 5 to 7.5 p. p. m., with zero residual, diminished the B. O. D. by 7.4 per cent.

(3) That increased dosage, within limits, results in increased oxidation. Sewage dosed with 8 to 9 p. p. m. of chlorine, with residuals from 0 to 0.1 p. p. m., indicated a B. O. D. reduction of 15.5 per cent.

(4) That the desirable dose is that amount which produces a residual of about 0.2 p. p. m. Samples which had received 10 to 15 p. p. m., with excess chlorine of 0.2 to 0.5 p. p. m., showed a decrease in B. O. D. of 42.7 per cent.

(5) That it is not economical to apply chlorine in excess of that necessary to give a 0.2 p. p. m. residual, as very little increased oxidation occurs with greater rates of dosage.

(6) That the B. O. D. reductions are permanent, as 15-day incubations showed relatively the same effect as 5-day samples.

(7) That in fully chlorinated sewage there is a retarding action on biological activity, as indicated by 1-day incubations. Chlorination would thus permit sewage to be carried downstream to adequate dilution before rapid decomposition sets in.

(8) That chlorination of sewage for B. O. D. reduction can be advantageously and economically applied in many cases, particularly where plants are overloaded, or slightly inadequate to protect stream quality, or to tide over dry periods of the year.

Acknowledgements

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1. "A Proposed Formula for Columns," T. F. Hickerson, May, 1928.
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